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(54) Title: METHOD FOR SEMICONDUCTOR PROCESSING USING MIXTURES OF HF AND CARBOXYLIC ACID

(57) Abstract

Method for semiconductor processing comprising etching of oxide layers, especially etching thick SiO₂ layers and/or last step in the cleaning process wherein the oxide layers are etched in the gas phase with a mixture of hydrogen fluoride and one or more carboxylic acids, eventually in admixture with water.

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METHOD FOR SEMICONDUCTOR PROCESSING USING
MIXTURES OF HF AND CARBOXYLIC ACID

Objects of the present invention

The present invention is related to improvements in semiconductor processing using HF formulated mixtures. The invention is more specifically related to methods making use of these mixtures in gas phase etching techniques of oxide layers, especially etching SiO_2 layers and in the so-called last step in the cleaning process.

State of the art and background of the invention

In the semiconductor processing, liquid HF mixtures are often used for etching thick SiO_2 layers or for etching chemical or native oxide layers.

For etching thick SiO_2 layers, usually buffered HF is used, which is a mixture of NH_4F and HF, in the liquid phase, generally as a solution in water.

Moreover, as a last step in the cleaning process, usually a diluted HF step is used.

Etching of bare silicon wafers in HF solution and/or a final etch in HF solution generally in combination with the RCA-process have been the object of many experimentation and publications.

The RCA-cleaning process for bare or oxidized silicon wafers is based on a two-step oxidizing and complexing treatment with hydrogen peroxide solutions: an

"HF-last cleaning" result in a Si-surface free of silicon oxide and passivated with hydrogen. However, the execution of this process with liquid HF mixtures is very susceptible to contamination.

5 The etch bath, chemicals, rinsing water and air ambient need to be very clean to achieve good results. Otherwise, severe contamination of the wafers with particles, metals and organic material can occur during the etching rinsing or drying process. "HF-last" processing with liquid
10 mixtures before gate oxidation is, therefore, still a point of controversy.

 As an alternative, the etching can be performed with HF mixtures in the vapour phase to prevent recontamination from the liquid and during rinsing and drying
15 of the wafers. By etching in the gas phase, recontamination from the liquid is omitted and the high susceptibility of the wafer for contamination during the drying stage is avoided. Furthermore, in the gas phase the etching of small features is facilitated while surface tension effects hamper this in
20 the liquid phase.

 Traditionally, the HF vapour etching is performed with a mixture of HF and H₂O vapours. This is described in US-A-4,749,440 of FSI for processes performed at near atmospheric pressures in a mode where the process gases are
25 continuous flowing, the so-called dynamic mode. Because of controllability problems with this process, the process was improved by performing it at substantially reduced pressures (600 Pa-2000 Pa) and applying a different procedure, the so-called static mode (see also US-A-5,167,761). Despite of
30 these improvements, the controllability of the process is still problematic.

 As an alternative, a method for etching silicon oxide by feeding anhydrous HF and alcohol vapour simultaneously into a reaction chamber is described in US-A-
35 5,022,961. However, this process suffers from the same limitations as the HF/water vapour process.

Aims of the present invention

The main aims of the present invention are to provide HF formulated mixtures operating in the gas phase which are more reliable than previous mixtures and which have an etching behavior which is very reproducible, which achieve good electrical results with respect to the oxides grown on oxide stripped silicon surfaces and which provide a reproducible and uniform process for etching of thick oxide layers.

Other objects and advantages of the present invention will appear to those skilled in the art from the detailed description of the invention to follow.

Main characteristic features of the invention

In order to achieve the intended aims, especially for semiconductor processing, the present invention proposes the use in the gaseous phase of mixtures of hydrogen fluoride and one or more carboxylic acids, possibly in admixture with water vapor, gases such as Ar, N₂, H₂, HCl or organic solvents such as alcohols, ketones, aldehydes and esters.

The carboxylic acid which is used is generally acetic acid (HAc). However, other carboxylic acids having one or more carboxylic functional groups (-COOH) may be used.

The pressures of HF and carboxylic acid in the gas phase may vary between 1 Pa and 10⁴ Pa. The specific partial pressures of respectively the HF vapour and the carboxylic acid vapour are 300 Pa and 600 Pa in etching techniques of SiO₂ and last step cleaning operations. Water can be added to enhance the etch rate or influence the selectivity of the etch rate for different types of oxides. When water vapour is present, the partial pressure of water may vary between 1 Pa and 10⁴ Pa.

Brief description of the drawings

In order to illustrate the state of the art and the advantages of the present invention, the following

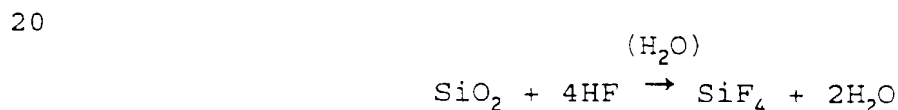
In these drawings:

- Figure 1 is a diagram of the etch depth as a function of the etching time in HF/H₂O vapours.
- Figure 2 is a liquid/vapour phase diagram of HAc/H₂O mixtures.
- Figure 3 is a diagram of the etch depth as a function of the etching time in HF/HAc vapours.
- Figure 4 is the interpretation of empirical model graphs.

10 Detailed description of an embodiment of the state of the art

Traditionally, the HF vapour etching is performed with a mixture of HF and H₂O vapours.

HF vapour can be generated by feeding a carrier gas like N₂ through a container with a mixture of liquid HF/H₂O. Alternatively, a bottle with anhydrous HF can be used as the source for HF vapour. In the latter case, it is found that anhydrous HF alone hardly etches SiO₂ at room temperature. The presence of H₂O is therefore preferred to initiate the reaction according to the overall equation:



The process can be performed in the static mode and in the dynamic mode.

In the static mode, the reactor is filled with a process gas up to a certain pressure and then the reactor is isolated for some time. Subsequently, the reactor is evacuated and the etch cycle can be repeated for a number of times. In the dynamic mode, a continuous flow of process gas is fed into the reactor which is maintained at a constant pressure.

However, it is generally recognized that it is difficult to control the etching reaction of SiO₂ with gaseous HF/water mixtures and to apply the etching process with good repeatability. The reproducibility can be seen from etching experiments as a function of time. If the reproducibility is good, then all experiments should follow a smooth evolution with time. In figure 1, the etch depth in

\dot{A} is shown as a function of etching time in a mixture of HF and H_2O vapour for one static etch cycle. It is clear from this figure that the reproducibility is poor since the etching processes do not follow a smooth time evolution.

5 Furthermore, the process is inflicted with an incubation time: under the chosen conditions, the first 10 minutes very limited etching occurs, see figure 1. The incubation time is found to depend on the pretreatment of the wafers. An RCA-cleaning just prior to the HF vapour etching
10 reduces the inhibition time. This is related to the concentration of adsorbed H_2O molecules on the oxide surface.

The onset of the etching process critically depends on the amount of molecules adsorbed on the silicon oxide surface. Water adsorption on the silicon oxide surface in its
15 turn is dependent on the number of OH centers already present on the surface and in this way is dependent on the quality of the oxide.

Uniform etching is another important criterion that determines the usefulness of the process. The uniformity
20 within the wafer and from wafer to wafer for a process using a batch of 6 wafers is represented in table 1. In column 5 of said table 1 the standard deviation within the wafer is shown. As can be seen from these values, the standard deviation within the wafer is not very good (32%). Also there
25 is quite a standard deviation from the wafer to wafer on the mean etch depth. In the presented case it is 27%. All these values show that the vapour HF/ H_2O mixture does etch the SiO_2 but has not a good performance regarding reproducibility, within wafer uniformity and wafer to wafer uniformity.

30 Detailed description of the preferred embodiments of the invention

The present invention is based on the consideration that the good reproducibility of the etching operation may be obtained by use in the gas phase of the new mixtures of

temperature. A catalyst is necessary to start the reaction.

Although H₂O can fulfil this role, the adsorption of H₂O on the silicon oxide surface is dependent on the number of OH centres already present and in this way on the quality of the oxide. The adsorption of organic molecules shows a strongly
5 reduced sensitivity for the amount of OH groups on the surface. Furthermore, the maximum density of adsorbed molecules strongly depends on the type of molecule. In table 2, the surface area occupied per adsorbed molecule is given for a number of different molecules. Obviously, acetic acid
10 occupies the smallest surface area.

Among the various carboxylic acids, acetic acid is a good choice regarding melting point (17°C), boiling point (118°C) and the shape of the carboxylic acid/H₂O liquid/vapour phase diagram. However, other carboxylic acids
15 having similar properties might be equally good or better choices.

The reaction involves the formation of SiF₄ and H₂O which are both gases at the used pressures :



The acetic acid only serves as catalyst ,

25

The etching of SiO₂ by HF generates water on the wafer surface. This water is, together with the acetic acid and the HF, assumed to be present in the form of a thin liquid film on the surface of the wafer and must be
30 transported away from the wafer surface by evaporation. In this respect the acetic acid/H₂O phase diagram for liquid/vapour equilibria is determining. This phase diagram is shown in figure 2. As shown in the figure, the vapour and liquid curves are close together. This means that the
35 composition of the vapour leaving the surface is close to the composition of the liquid on the surface. The shape of the curve implies that the vapour is even somewhat more water rich than the liquid. Consequently, the water generated on the surface can easily be transported away. For other organic

liquids like alcohols, acetone, the liquid and vapour curves are far apart resulting in a large difference between composition of the liquid and the vapour. Furthermore, for the mentioned materials the shape of the curves is such that the vapour is substantially less water rich than the liquid. Hence the water is not easily removed from the surface, giving rise to a strong increase in surface water concentration in the course of the etching process. This results in a fundamental controllability problem of the etching process which is not present with carboxylic acids and especially acetic acid.

Figure 3 illustrates as an example the etching behaviour of a mixture in accordance with the invention. The etch depth as a function of time is shown when SiO_2 is etched in an HF/acetic acid gas phase mixture. As can be seen, the reproducibility is very good since the time evolution is very smooth. It must be noted that the processes which were run to generate this graph were run over different days and still the measured etch depths fall on a smooth curve showing the high degree of reproducibility.

Acetic acid appears to have a similar catalytic effect on the HF etch process as H_2O because substantial etch rates are achieved. For the static etch mode, a perfectly proportional relation between etch time and etch depth is found until for large times the curve flattens out because of depletion effects. No incubation time can be observed.

In table 3, the etching uniformity of this process is examined in the same way as the HF/ H_2O vapour mixture. Good uniformity within the wafer (average standard deviation 6.05%) and good uniformity from wafer to wafer (standard deviation 3.5%) is achieved.

This shows that the process HF vapour/carboxylic acid yield much more uniform and reproducible etching than the HF/ H_2O process.

influence of acetic acid on the etching process is

substantial. The acetic acid partial pressure provides a means to reduce the variation in etch depth over the wafer and over the batch and improves the controllability of the process.

5 These results relate to the etching of silicon oxide formed by the thermal oxidation of silicon in dry oxygen or in water vapor. For silicon oxide films formed by chemical vapor deposition the etch rate is typically higher. In table 5 the etch rate selectivity which is the ratio of
10 the etch rate of silicon oxide formed by thermal decomposition of Tetra Ethyl Ortho Silicate (TEOS) and the etch rate of silicon oxide formed by thermal oxidation of silicon is given for two process :

- 1) a liquid mixture of 0.5 vol % HF in H₂O,
- 15 2) a vapor mixture of HF and acetic acid according to the present invention.

Densification of the TEOS oxide after deposition substantially reduces the etch rate but the etch rate still remains higher than that of thermal oxide. In general it is
20 to be preferred that the selectivity is close to 1 to allow a controlled removal of different types of oxides that can simultaneously be present. The performance of the HF/acetic acid mixture is in this respect approximately equivalent to the liquid mixture.

25 Tests for particle contamination showed in the HF/acetic acid vapour etch process an average increase of 46 light point defects (0.12 μ m Latex Sphere Equivalent) per 125 mm wafer, which is very low.

The invention will be further elucidated referring
30 to the following example.

Example

The method according to the subject invention was realized in a reaction chamber equipped with three inlets:
35 one for anhydrous HF, one for acetic acid and one for a dry N₂ purge. The gas lines for HF and acetic acid are heated to approximately 50°C. A metal bottle with anhydrous HF at room temperature is used as source for the HF vapour. Acetic acid

is supplied from a quartz bottle which is maintained at 45°C. The flows of the vapours are controlled by Mass Flow Controllers. The inlet lines were combined at a distance of about 50 cm above the reactor. The reactor and associated
5 equipment according to the invention was made from materials chemically resistant to the reactive HF/carboxylic acid/water mixtures. The reactor and some other parts were made of stainless steel and coated with Halar®. The wafer boat and the part of the gas lines that is exposed to the vapour
10 mixtures were made of Monel. The gas lines that are exposed to only one of the individual vapours is made of electropolished stainless steel. A proper choice is of great importance as the entire purpose of the etch is defeated if the removal of the native oxide would lead to an excessive
15 generation of particles from either the reactor walls, the wafer support structure, the gas feed lines, etc.

The reactor is loaded with a batch comprising 4-25 silicon wafers, being kept at ambient temperature. Subsequently, the reactor chamber loaded with wafers is
20 evacuated. After evacuation, the valve to the pump is closed. After this the inlet of HAc vapour is opened and HAc vapour is injected into the reactor up to a pressure of 600 Pa. Then the HAc inlet is closed. After this, the HF inlet is opened, HF vapour is injected into the reactor up to a total pressure
25 of 900 Pa (partial HF pressure is 300 Pa) and the HF inlet is closed. The wafers are subsequently kept isolated in the system for some time, in this case 200 seconds. After said time interval has elapsed, the pump valve is opened and the process gases are pumped away. Then the reactor is purged
30 with dry N₂ to atmospheric pressure.

The results of this procedure were already presented in table 3.

Although the invention is described referring to

used.

Table 1Etching results in HF/H₂O vapour

Wafer	Minimal etch depth (Å)	Maximal etch depth (Å)	Mean etch depth (Å)	Standard deviation
1	38	150	85	38
2	26	106	50	32
3	38	104	61	26
4	38	113	65	26
5	18	97	43	37
6	22	89	45	34

Table 2

Surface area occupied by different molecules adsorbed on silicon dioxide

Molecule	Formula	Surface area/molecule
		(Å**2)
Acetic Acid	CH ₃ COOH	9.1
Water	H ₂ O	12.5
Nitrogen	N ₂	16.4
Methanol	CH ₃ OH	18.0
Ethanol	C ₂ H ₅ OH	18.0
n-Propanol	C ₃ H ₇ OH	21.3
Hexene	C ₆ H ₆	55.0

Table 3

Etching results in HF/HAc vapour

Wafer	Minimal etch depth (Å)	Maximal etch depth (Å)	Mean etch depth (Å)	Standard deviation
1	71	97	84	5.8
2	75	100	89	7.7
3	72	97	86	6.2
4	71	91	82	4.6

Table 4

Experimental matrix to investigate the HAC/HF parameter space

P_{HF}	P_{HAc}	Etch depth	p-p deviation	w-w deviation	contact angle
Pa	Pa	Å	%	%	°
200	200	83.5	15.9	2.4	59.8
400	200	200.5	13.4	7.6	62.0
200	800	181.6	7.7	4.9	61.1
400	800	395.3	6.7	1.6	62.9
300	500	216.1	11.6	1.7	58.1
300	200	155.9	14.5	4.4	58.9
200	500	148.1	12.6	1.4	58.8
300	800	288.7	10.2	2.6	62.8
400	500	299.7	12.1	2.9	62.5

Table 5

Etch rate selectivity for TEOS oxide/thermal oxide

Mixture	As-deposited	Half densified	Densified
liquid, 0.5 vol% HF in H ₂ O	8.5	5.0	1.4
vapor, 300 Pa HF, 600 Pa HAc	12.0	4.1	1.4
As-deposited TEOS oxide	725 °C, low pressure		
Half densified TEOS oxide			

CLAIMS

1. Method for semiconductor processing comprising etching of oxide layers, especially etching thick SiO_2 layers and/or last step in the cleaning process wherein the oxide
5 layers are etched in the gas phase with a mixture of hydrogen fluoride and one or more carboxylic acids.

2. Method according to claim 1 wherein the carboxylic acid is acetic acid.

3. Method according to any one of the claims 1 or
10 2 wherein the oxide layers are treated in admixture with water.

4. Method according to any one of the claims 1-3 wherein the partial pressures of HF and the carboxylic acid are comprised between 1 Pa and 10^4 Pa.

15 5. Method according to any one of the claims 1-5 wherein water is added with a partial pressure comprised between 1 Pa and 10^4 Pa.

6. Method according to any one of the claims 1-4 wherein the partial pressures of HF and the carboxylic acid
20 are comprised between 100 Pa and 1000 Pa.

7. Method according to any one of the claims 1-5 wherein the partial vapour pressure of HF is 300 Pa and the partial vapour pressure of carboxylic acid is 600 Pa for both the etching of thick SiO_2 layers and as a last step in the
25 cleaning process.

8. Method according to any one of the claims 1-7 wherein the etching is performed in the static mode.

9. Method according to any one of the claims 1-7 wherein the etching is performed in the dynamic mode.

30 10. Method according to any one of the claims 1-9 wherein the etching is performed at a temperature between 0°C and 400°C .

11. Method according to any one of the claims 1-10 wherein the etching is performed at room temperature.

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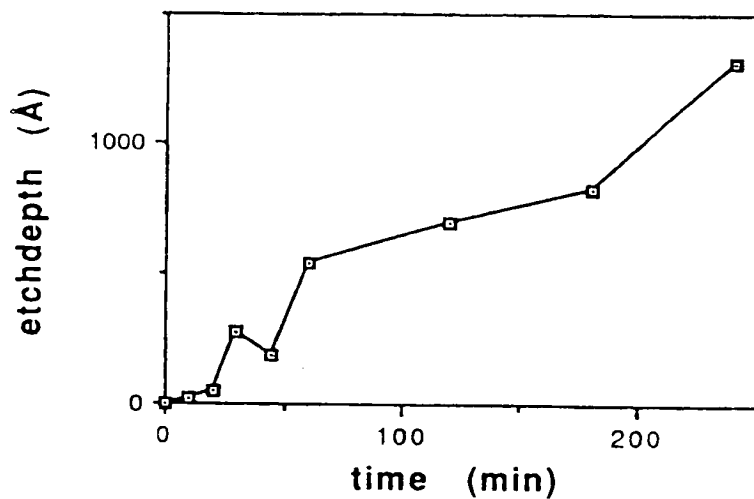
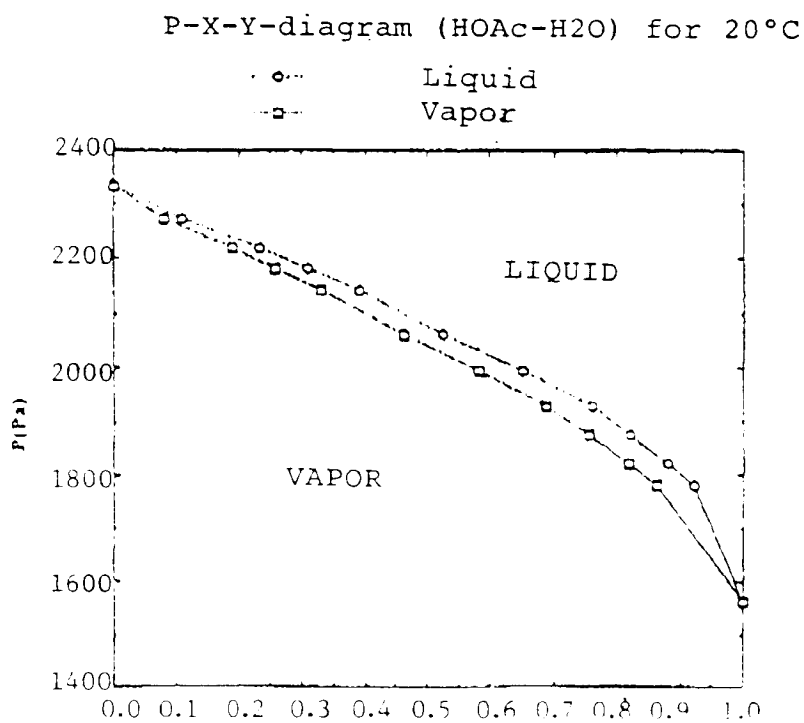


Fig. 1 Etch depth as a function of etching time in HF/H₂O vapor.



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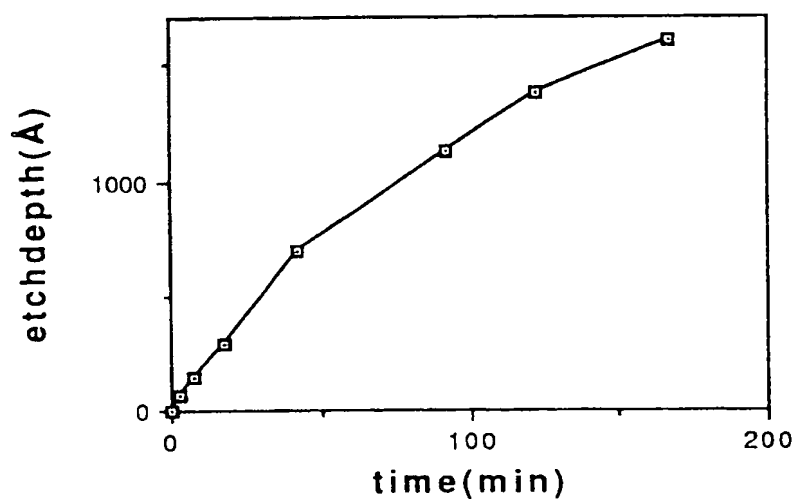


Fig. 3 Time evolution of etch depth for a HF/Acetic acid vapor mixture

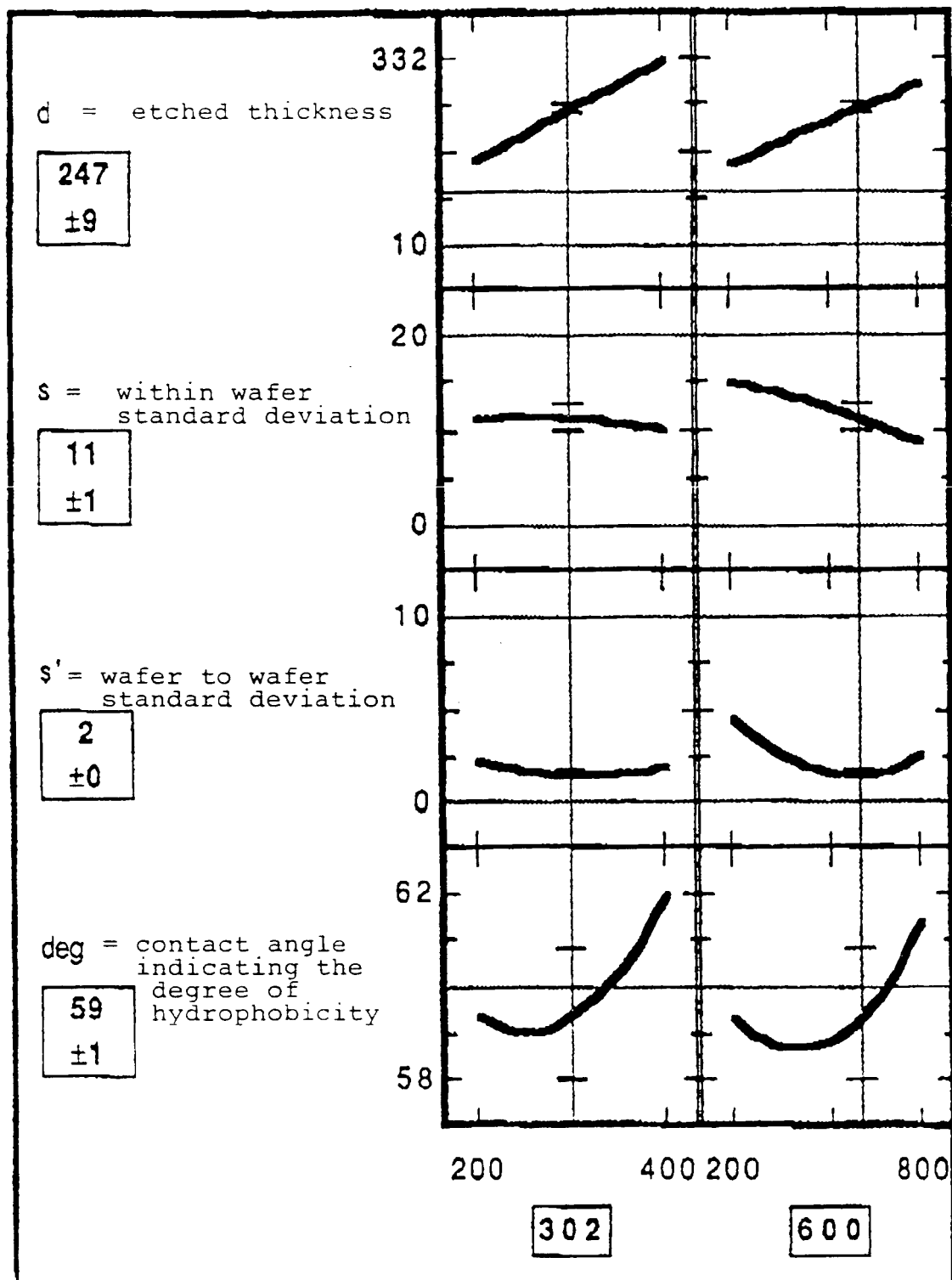


Fig. 4

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 94/01534

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 H01L21/311 H01L21/306

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol.138, no.6, June 1991, MANCHESTER, NEW HAMPSHIRE US pages 1799 - 1802 WONG ET AL 'characterization of wafer cleaning and oxide etching using vapor phase hydrogen fluoride' see page 1800, left column, paragraph 3 - page 1801, left column, paragraph 1 ---	1,9-11
A	EP,A,0 488 198 (TANAKA) 3 June 1992 see abstract ---	1
A	US,A,5 022 961 (IZUMI ET AL) 11 June 1991 cited in the application see abstract --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Intern. Application No.

PCT/94/01534

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 536 752 (ROBERTS ET AL) 14 April 1993 see claims 1,4 ---	1-7,9-11
A	EP,A,0 536 747 (ROBERTS ET AL) 14 April 1993 see claims 1,5 ---	1-7,9-11
A	DE,B,13 02 175 (NICKL) 23 July 1970 see column 2, line 6 - line 10; claims 1,5 -----	1,3,8, 10,11

INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent Application No.

PCT/EP 94/01534

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0488198	03-06-92	JP-A- 5041367 US-A- 5279705	19-02-93 18-01-94
US-A-5022961	11-06-91	JP-A- 3129731 JP-A- 3204932	03-06-91 06-09-91
EP-A-0536752	14-04-93	US-A- 5213622	25-05-93
EP-A-0536747	14-04-93	US-A- 5213621	25-05-93
DE-B-1302175	23-07-70	NONE	